PY G345/4. 10/7
no. 57
c. 2

Information Circular 57

1967

A METHOD FOR DETERMINING POST-DEPOSITIONAL ALTERATION IN UNDERCLAYS AND ASSOCIATED LITHOLOGIES

Michael G. Jaron

COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF INTERNAL AFFAIRS
John K. Tabor, Secretary

BUREAU OF
TOPOGRAPHIC AND GEOLOGIC SURVEY
Arthur A. Socolow, State Geologist

PENNSYLVANIA STATE LIBRARY
DOCUMENTS SECTION

Digitized by the Internet Archive
in 2016 with funding from
This project is made possible by a grant from the Institute of Museum and Library Services as administered by the Pennsylvania Department of Education through the Office of Commonwealth Libraries

https://archive.org/details/methodfordetermi00jaro

INFORMATION CIRCULAR 57

A METHOD FOR DETERMINING POST-DEPOSITIONAL ALTERATION IN UNDERCLAYS AND ASSOCIATED LITHOLOGIES

by Michael G. Jaron
Staff Geologist

PENNSYLVANIA GEOLOGICAL SURVEY
FOURTH SERIES
HARRISBURG

1967

Copyrighted 1967

by the

Commonwealth of Pennsylvania

Quotations from this book may be published if credit is given to

the Pennsylvania Geological Survey

ADDITIONAL COPIES

OF THIS PUBLICATION MAY BE PURCHASED FROM

CAPITOL BOOK STORE, ROOM 54, MAIN CAPITOL BUILDING

HARRISBURG, PENNSYLVANIA 17125

CONTENTS

	Page
Abstract	1
Introduction	1
Acknowledgments	3
Procedure	3
Description of section	5
Mica polymorphs and size analysis of titanium-bearing minerals	7
Discussions	8
Conclusion	13
References	13

FIGURES

		Page
FIGURE 1.	Method of drawing tangents to symmetric and asymmetric (001) illite X-ray reflections	4
2.	Graph showing relative limonite content, percent TiO_2, and (001) illite line broadening as a function of depth	10
3.	Graph showing relative limonite content and (001) illite line broadening to percent TiO_2 as a function of depth	11

A METHOD FOR DETERMINING POST-DEPOSITIONAL ALTERATION IN UNDERCLAY AND ASSOCIATED LITHOLOGIES

by

Michael G. Jaron

ABSTRACT

A detailed vertical sample of argillaceous and carbonate lithologies underlying a coal seam was studied in order to develop criteria for distinguishing between sediments that have undergone post-depositional alteration (both pedologic and nonpedologic) and sediments that have remained largely unaltered.

Post-depositional alteration is suggested by zones showing limonite concentrations, and an increase with proximity to the surface of percent TiO_2 and line broadening of the (001) illite X-ray reflection.

Unaltered noncarbonate clay lithologies showed a constant ratio of illite line broadening (in degrees of angular spread) to percent TiO_2 of about 10. Weathering and/or changes in the character and rate of sedimentation tend to change this ratio.

INTRODUCTION

The lithologies underlying coal seams consist usually of a diverse group of carbonate, argillaceous and sandy sediments. The origin of these sediments has been the subject of considerable controversy. Two major modes have been proposed: 1) a residual origin which stresses their similarity to soil horizons; and 2) a transported origin which emphasizes their similarity to detrital materials.

The residual origin of underclays and associated seat rocks has been discussed by Huddle and Patterson (1961). They considered the underclay complex (i.e. underclays and interstratified sediments) to be seat rocks formed *in situ* by the alteration of sediments in a swamp environment. The transported detrital origin of underclays has been discussed by Grim and Allen (1938) and Schultz (1958). They suggested that alteration actually occurred at the source area during detritus transport, previous to deposition, and that little or no post-depositional alteration has occurred.

One of the difficulties in postulating an *in situ* weathering origin for lithologies underlying coal strata is the reported absence of soil profiles (Grim and Allen, 1938). However, the preservation of a fossil soil does not commonly happen (Nikiforoff, 1943). This is especially true for waterlogged soils which have formed in a reducing environment where subsequent dewatering and oxidation could easily destroy the original pedological features. Compaction of the profile as it undergoes lithification, and truncation by erosional agents may render a fossil unrecognizable. Recognition of fossil soils is further complicated by the fact that nonpedological processes occurring at depth (for example, ground-water alteration) may result in the formation of units that look similar to soils but which, in fact, are not. Because these units may resemble a leached soil horizon, it is possible for an altered transported sediment to assume the appearance of a residual soil. In regard to the above, an analysis of the lithologies below the Upper Freeport coal was undertaken in the hope that the results of such an analysis would be helpful in making a distinction between sediments that had undergone post-depositional alteration (both pedologic and nonpedologic) and sediments that had remained largely unaltered. The results of this analysis are the subject of this report.

A soil is formed largely from the physical and chemical breakdown of minerals. Some minerals are more resistant to the breakdown process than others, and their presence serves to roughly indicate the intensity of weathering. Plots of relatively stable indicator minerals as a function of depth can be used to calculate the extent of soil formation.

Muscovite is an example of an indicator mineral. As muscovite is weathered it decreases in grain size and undergoes chemical changes, such as potassium loss. The latter process may cause structural strain and disorder within the muscovite crystal lattice. Such muscovite, termed illite, becomes more "illitic" as weathering proceeds. One method used to gauge the degree of "illitization" of muscovite is the determination of the amount of line broadening shown by measuring the angular peak breadth of the (001) illite X-ray reflection (Lapham and Jaron, 1964; see also Procedure, this paper). Van Houten (1953) and Harrison and Murray (1959) report that illite from soils and zones of weathering is deficient in K_2O. Weaver (1965) infers that a decrease in K_2O contributes to illite broadening. In a study of the underclays of South Wales, Wilson (1965) reports that samples collected from directly beneath coals had the most broad and diffuse (001) illite X-ray reflections. The above data suggest, therefore, that the (001) illite line-broadening phenomenon may be used to measure relative differences in degree of post-depositional alteration within a sampled profile.

Rutile and anatase are also indicator minerals. They occur when titanium-bearing minerals such as sphene and ilmenite alter after extensive weathering. Concentrations of these secondary titanium-bearing minerals are characteristic of residual weathering zones. Many clays and shales associated with coal strata have an unusually high TiO_2 content (Huddle and Patterson, 1961) and are evidently high in TiO_2 resistates. Thus TiO_2 content, chosen as a second variable may also be used to indicate the relative intensity of post-depositional alteration in lithologies associated with coal.

When iron-bearing minerals such as pyrite and siderite are present they are commonly oxidized to form limonite. Concentrations of limonite, ascertained qualitatively in the field by the relative degree of staining and by the occurrence structures such as concretions and nodules, were chosen as a third criterion indicative of leaching and/or oxidation.

Theories presented in this paper do not necessarily comment on the origin of all underclays; however, the method of study may apply to future work.

ACKNOWLEDGMENTS

The author is extremely grateful to Dr. Davis M. Lapham for his stimulating discussion and advice at all stages of this work.

Dr. Richard L. Weiss rendered invaluable help in reading the manuscript and suggesting improvements in presentation.

The writer is also deeply indebted to Dr. M. L. Jackson, Dr. David K. Webb, Jr., and Mr. Albert Glover for critically reading the manuscript.

PROCEDURE

A vertical column of samples was collected from directly below the Upper Freeport coal in the high wall of a freshly bulldozed strip mine, in Clearfield County, Pennsylvania. Samples were collected wherever changes in lithology, color, and texture were observed. The maximum sample interval was 6 inches. A qualitative mineral analysis was conducted on each sample with the aid of a Norelco X-ray Diffractometer using Ni-filtered Cu radiation and a scanning speed of 1 degree 2θ per minute. Quantitative determinations of percent TiO_2 were conducted with the aid of a Norelco X-ray Spectrograph using an air path, W radiation, and a scanning speed of $\frac{1}{4}$ degree 2θ per minute. Seventeen under-

clays previously analyzed by a wet chemical method for another study (O'Neill, and others, 1965) served as standards. TiO_2 content was plotted as a function of the peak height of TiKα emissions at 86.08 degrees 2θ. Accuracy was estimated to be plus or minus 0.05 percent.

Line broadening of the (001) X-ray reflection of illite was measured by drawing a tangent to each side of the reflection and measuring the angle made by the tangents with a protractor. Using this technique, low angle shoulders from reflections greater than 11Å (probably the result of interlayered clay minerals) are effectively cut out and do not enter into illite line broadening measurements. Figure 1 illustrates the method used to draw the tangents for both the symmetric and the asymmetric reflections. Three individual, randomly oriented, back-filled samples were run for each interval sampled. Accuracy was estimated to be plus or minus 1 degree of angular broadening. Samples were run with the X-ray diffractometer rate meter set at a scale factor of 4, a multiplier of 1, and a time constant of 4. Scanning speed was 1 degree 2θ per minute at 40.3 kilovolts and 17 milliamperes. Where the presence of weak intensities required a scale factor of 2, the angular peak breadth was recalculated to a scale factor of 4 by dividing the measured angle by 2. The validity of this manipulation was substantiated by the author in experimentation prior to this study. For direct comparison of these data with previous illite line broadening measurements of the clays and shales of Pennsylvania (Lapham and Jaron, 1964; O'Neill and others, 1965), the angular measurements cited in this report should be multiplied by two.

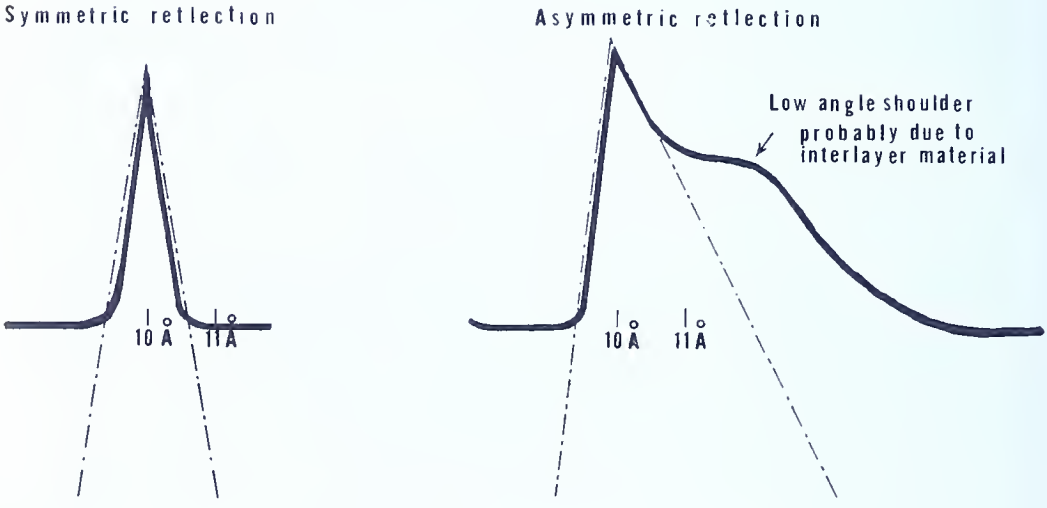

FIGURE 1. Method of drawing tangents to symmetric and asymmetric (001) illite X-ray reflections.

Five samples were selected for additional analyses. Samples 77-83, 83-85, 85-91, 91-97, and 97-99 were mixed with water and disaggregated with a rubber pestle (sample numbers indicate depth range, in inches, below the coal). These samples were chosen because of the relative ease with which they disaggregated. The disaggregated samples were sieved to separate the coarse grain sizes from the fine. Both grade sizes were then analyzed for TiO_2 and were X-rayed to determine the muscovite structural polymorph constituting the illite. Sample 97-99 was treated according to a method outlined by Raman and Jackson (1965) in order to ascertain the presence of rutile and anatase.

DESCRIPTION OF SECTION

The section sampled was divided into four units on the basis of similar lithology. Twenty-one feet of sediment consisting of a one-inch-thick carbonaceous shale, sandstones, and siltstones lie below the lowest sample collected and the next coal, the Lower Freeport coal.

Lithologic Unit I extends from 0 to 25 inches below the coal and consists largely of claystone and shale. The uppermost half inch is a carbonaceous shale which grades into a carbonaceous claystone. The top of the carbonaceous claystone spalls into thin discontinuous sheets parallel to formation contacts and is here referred to as an incipient layered claystone. Below this, to a depth of 12 inches the claystone becomes extremely slickensided; however, from 12 to 23 inches the slickensides diminish and incipient layered claystone prevails. Below the claystone shale appears. Carbonaceous matter, including *Stigmaria* rootlets and carbon films, decreases in abundance downward, causing the color to change from grayish black (N2) to medium olive gray (5Y5/1). The (001) angular peak breadth and the percent TiO_2 also generally decrease downward, but at a zone of limonite accumulation, approximately 23 inches below the coal, both increase (Fig. 2).

Lithologic Unit II extends from 25 to 57 inches below the coal and consists of a limonitic hardpan, clay, and shale; limestone; and a carbonate clay and shale. Although the unit is predominantly composed of carbonate lithologies, the upper 14 inches, unlike the rest, contains little or no carbonate minerals and is characterized by abundant limonite. The uppermost 2 inches is a fine-grained, yellow-gray (5Y 7/2) shale containing extensive limonite and a gnarled tuberose limonite structure. This structure consists of thin concentric layers of limonite (in some parts

admixed with clay) with a maximum diameter of 1 inch and a maximum length of 4 inches. Below the yellow-gray shale is a chambered hardpan 6 inches thick made up largely of quartz, limonite, and a minor amount of gibbsite. Original carbonate that might have been present has been leached out. The ellipsoidal hardpan chambers are elongate parallel to formation contacts. The chamber walls probably represent either accretionary material or substances resistant to leaching.

Below the hardpan is a very soft, limonite-bearing plastic clay composed of chlorite-vermiculite-montmorillonite (undifferentiated), illite, and a minor amount of kaolinite. This clay becomes less plastic with depth, and towards its base contains argillaceous limonite nodules and a decreasing amount of chlorite-vermiculite-montmorillonite (undifferentiated). Although the contact between the hardpan and the underlying soft clay is sharp, the hardpan does contain shale partings and clay accumulations scattered throughout. Mineralogically these shale partings and clay accumulations are somewhat different from the soft clay below, in that they lack kaolinite, but contain gibbsite and an illite which exhibits a greater angular peak breadth.

Below the soft clay is a 2-inch zone of thinly laminated, dolomite-bearing, limonitic shale. Below this is a sideritic claystone with a small amount of dolomite. The contact between the limonitic shale and sideritic claystone is undulatory. The top of the sideritic claystone contains small ellipsoidal limonite concretions with goethite cores which are elongated approximately perpendicular to the unit contacts. Their long and short axes are, respectively, about 3 mm by 1 mm.

Fossiliferous, ostracod- and worm tube-bearing, fresh-water limestone occurs below the sideritic claystone. This limestone is composed largely of calcite, although minor amounts of pyrite, clay minerals, and quartz are also present. It does not have, however, a sufficient quantity of illite to attempt an accurate measurement of line broadening.

Below the limestone is a calcite-bearing, fine-grained shale which contains ostracods and worm tubes. It has a fetid odor when crushed, shows a minor amount of slickensides, and is profusely spotted with limonite. This shale also shows extensive development of tuberous limonite structures. The bedding of the shale follows the contour of these structures, and they may be of organic origin, the result of ground-water precipitation or both.

Samples from this unit (Lithologic Unit II) are generally low in TiO_2 (Fig. 2). However, these samples which have been altered (i.e. highly limonitic) or which are argillaceous have higher TiO_2 values. For example, the limonitic soft clay below the hardpan has the highest TiO_2 content of any lithology in this unit. The extensive amount of alteration (estimated visually by the concentration of limonite and the

leached aspect of the rocks) and the paucity of illite in this unit precluded the establishment of accurate line broadening measurements for many of the samples in this unit.

Lithologic Unit III extends from 57 to 63 inches below the coal and is composed entirely of semiflint clay. The semiflint clay of this unit is a hard, gray rock (Munsell color chart designation N6.5) exhibiting a hackly fracture. The upper contact is slickensided while the lower contact is undulatory, as if the clay were deposited on an erosional surface. This unit has a TiO_2 content of 1.26 percent, which is noticeably higher than that for the lithologies immediately above and below. Similarly, the illite angular peak breadth is larger, about 16.0 degrees.

Lithologic Unit IV extends from 63 to 100 inches below the coal and is largely composed of claystone and shale. The upper 8 inches is a calcite-bearing claystone, the top part of which is extensively stained by limonite. The upper contact is an undulatory erosion-like surface that is moderately stained by limonite.

Below the calcite-bearing claystone is a series of carbonate-deficient claystones and shales. These claystones are slickensided and contain carbonaceous material. Near the base of this series, abundant friable limonite is evident.

There is some similarity between Unit IV and Unit I; however, Lithologic Unit I lacks carbonate, exhibits much less limonite, has a fresh appearance, and shows an orderly downward variation from carbonaceous to noncarbonaceous claystone.

The TiO_2 content and the angular peak breadth of Lithologic Unit IV are greater toward the base which is marked by pervasive limonite suggestive of ground-water activity.

MICA POLYMORPHS AND SIZE ANALYSIS OF TITANIUM-BEARING MINERALS

Five samples were selected for special analyses. Samples 77-83, 83-85, 85-91, 91-97, and 97-99 were first disaggregated and sieved. About 80 to 88 percent of each sample passed through the 325-mesh sieve. Analyses of the +325- and −325-mesh fractions by X-ray fluorescence show that the titanium is largely concentrated within the −325-mesh fraction. X-ray powder camera photographs of claystone sample 97-99 (which was treated with HCl and HF) show that anatase and rutile are present.

Diffractometer analyses for the various muscovite polymorphs show that 2M, 1M, and possibly 1Md structures are present, and that the 2M polymorph is dominant, with the 1Md structure increasing in abundance as the grain size decreases. Because the 2M structural polymorph apparently indicates a high-temperature origin (Yoder and Eugster, 1954), most of the illite in these samples is probably of detrital origin and not a low-temperature authigenic form. Although some of the illite has a low-temperature 1M and 1Md structure and may, in fact, be authigenic in origin, the claystones in which this illite occurs probably formed in an acidic swamp environment. This environment is presently acidic and apparently has always been so (Huddle and Patterson, p. 1652, 1961). As such, it is not conducive to the formation of illite, but, on the contrary, might lead to its breakdown. Kaolinite, a common "underclay" mineral, would seem to be the logical end product of illite weathering in an acidic environment. Carr, Grimshaw, and Roberts (1953) separated a micaceous mineral from a Yorkshire fireclay. Under the polarizing microscope this material (also having a 2M structure, according to Smith and Yoder, p. 229, 1956) showed signs of alteration. X-ray diffraction powder photographs and chemical analysis showed the mineral to be a mixture of potassium-deficient, hydrous mica and kaolinite. This implies that the illite to kaolinite transformation is reasonable. Velde (1965) has shown in the laboratory that the kaolinite to muscovite reaction proceeds rapidly; perhaps, given enough time, the reaction is reversible in nature.

In the –325-mesh fraction the (001) illite peak generally lacks a low angle shoulder, rendering it sharper and easier to measure. The amount of angular peak breadth in this fine fraction is the same as in the unsized sample, probably because in all the samples the –325-mesh fraction comprises at least 80 percent of the total sample. No relationship has been established between grain size and angular peak breadth; however, in a study of K-Ar ages of Pennsylvanian underclays, Albrecht Hofman, a graduate student at Brown University (personal communication) reports that as grain size decreases the (001) illite reflections become broader.

DISCUSSIONS

Limonite.—Limonite varies in abundance throughout the section sampled (Fig. 2). As observed in the field, limonite is least abundant in Lithologic Units I and III, is common in Unit IV, and is a major constituent of Unit II. Concentrations of limonite may result from postdepositional ground-water alteration. This is evidenced by the limonite concretions whose long axes are perpendicular to formation contacts.

Those areas show notable limonite concentrations, illite line broadening, and to a lesser degree a relatively high TiO_2 content. A case in point is the base Lithologic Unit IV. With the exceptions of its decomposed weathered aspect and its unusual concentration of limonite, sample 99-100, at the base of Lithologic Unit IV, is similar in lithology to sample 6-12 of Lithologic Unit I. However, the former has an angular peak breadth of 16 degrees, plus or minus 1 degree, and a TiO_2 content of 2.10 percent, plus or minus 0.5 percent while the latter has an angular peak breadth of only 12 degrees, plus or minus 1 degree, and a TiO_2 content of 1.14 percent, plus or minus 0.5 percent.

Lithologic Unit II contains limonite structures which, if they are not a part of an ancient soil profile, are the result of soil-forming processes. For example, the hardpan and underlying soft clay are most easily explained as the result of leaching and illuviation. The presence of easily leached but unaltered limestone 9 inches below the soft clay and relatively unaltered underclay above the hardpan suggests that leaching was a near-surface or surface phenomenon that ceased soon after deposition of the Unit I underclay. In addition, the argillaceous limonite nodules at the base of the soft clay appear to represent the parent material from which the hardpan and the soft clay were derived. Also, irregular ellipsoidal limonite concretions with goethite cores occur between the dolomite-bearing shale and the underlying sideritic clay. These concretions are elongated in a direction perpendicular to formation contacts and most probably represent a stalactitelike advance of downward leaching. Finally, the tuberose limonite structures at the top and base of the unit are of uncertain origin; however, structures of similar shape and composition occur in waterlogged horizons of ground water gleys. (Blumel, 1962 as cited by Brewer, p. 254, 1964.)

TiO_2 and Illite Line Broadening.—The TiO_2 values reported in Figure 2 are in effect the amount of TiO_2 in the sample holder as "seen" by the X-ray spectrograph. In some cases this amount of TiO_2 differs from that of the raw sample. For example, sample 27-33, a porous hardpan, undergoes an increase in apparent density when it is powdered and tightly packed into the sample holder. For this sample the reported TiO_2 value per original unit volume is higher than that for the raw sample. Time did not permit an accurate estimate of the amount of apparent density change that a specific lithology undergoes during sample preparation.

Graphs similar to the one in Figure 2 (i.e., graphs showing the variation of stable constituents as a function of depth) are used by pedologists to estimate gains and losses at the various soil horizons during soil formation (Brewer, Chapter 4, 1964). These graphs are helpful in determining the parent material from which a given soil horizon may have developed. The parent material can be identified when a stable constituent curve

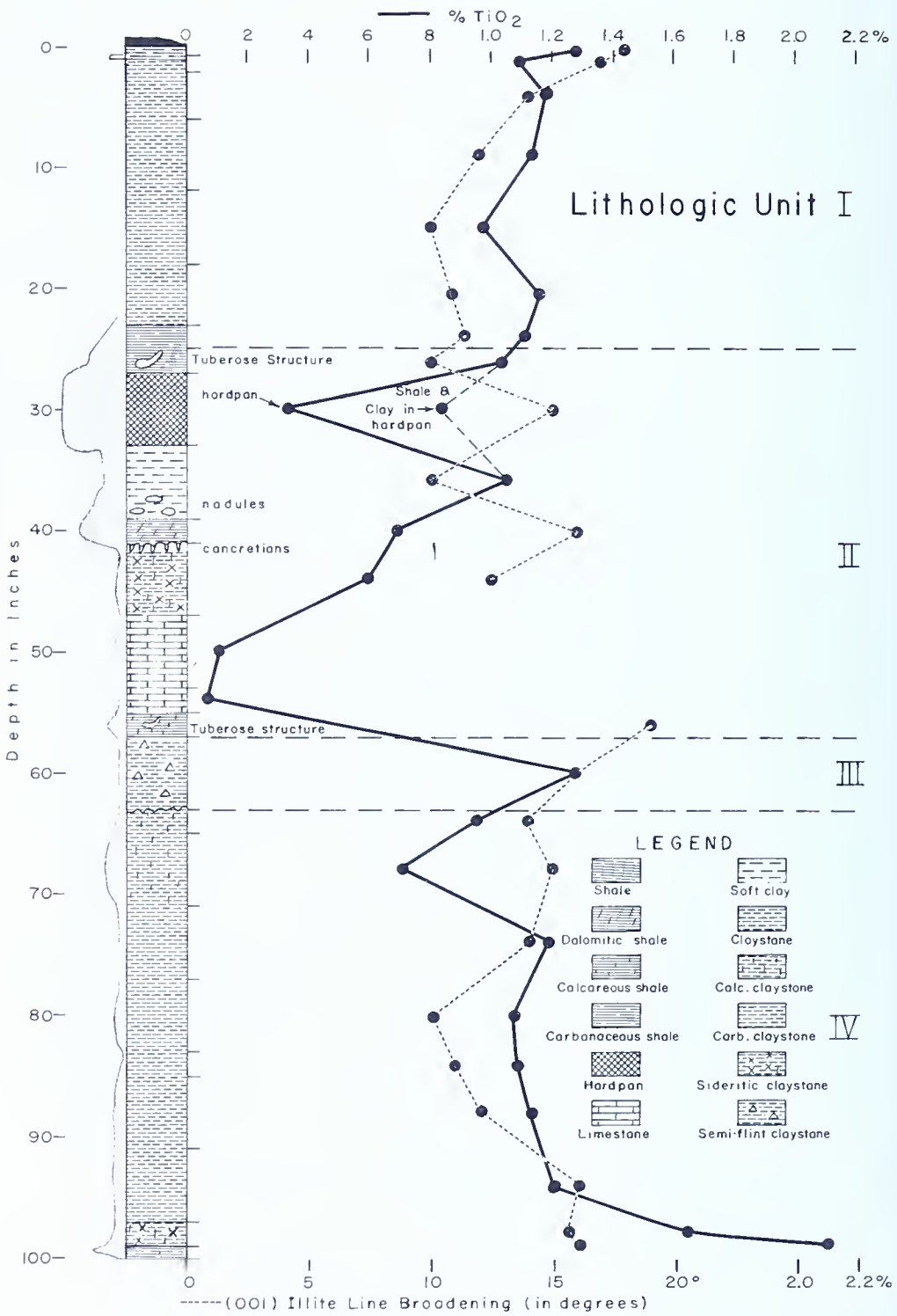

FIGURE 2. Graph showing relative limonite content, percent TiO_2, and (001) illite line broadening as a function of depth.

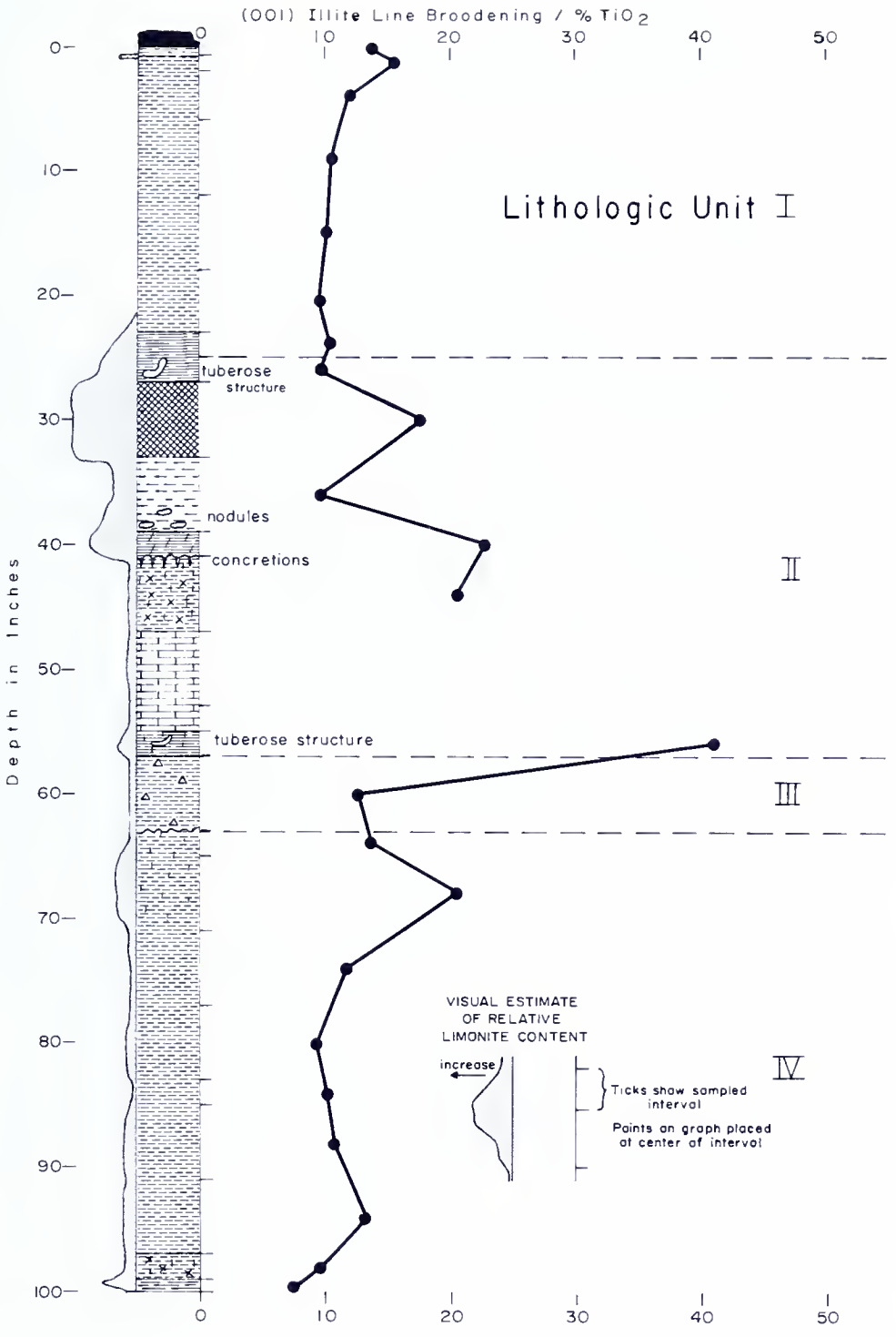

FIGURE 3. Graph showing relative limonite content and (001) illite line broadening to percent TiO_2 as a function of depth.

approaches parallelism with the depth axis. If the parent material is not uniform, this ideal condition may not be realized. Zones of weathering and changes in sedimentation are shown as points of inflection or maxima and minima on the curve.

Generally, where alteration has occurred, the TiO_2 content increases and the (001) illite reflection broadens (Fig. 2). In the case of Lithologic Unit I, the underclay, where most of the alteration is probably not the result of subsurface ground-water action, there is an illite peak breadth and a TiO_2 maximum at the upper, more carbonaceous part of the unit. This maximum may be the result of the weathering action of plants in a paludal environment (Keller and Frederickson, 1952).

A graph showing the ratio of (001) illite line broadening to percent TiO_2 as a function of depth is presented in Figure 3. It can be seen from this graph that in the section sampled, unaltered, noncarbonate clay lithologies have a nearly constant ratio of about 10. Weathering and changes in the character and rate of sedimentation tend to change this ratio such that the percent TiO_2 increases at a slower rate than the angular peak breadth. In sample 99-100 (99 to 100″ interval, see Figs. 2 and 3), however, TiO_2 has apparently increased at a faster rate, which may be related to the more intense alteration (concentration of limonite, weathered aspect, and the like) that this sample has undergone, or to an originally higher TiO_2 content. Carbonate clay lithologies generally have a higher and a more variable ratio than noncarbonate clay lithologies. This apparently is an expression of the varying TiO_2 content of these carbonate rocks, and seems to be a function either of the relative ease with which they can be leached or of dilution of the TiO_2 content by carbonate deposition.

In addition, the graph in Figure 3 which shows the ratio of resistate constituents as a function of depth, imparts to Lithologic Unit I a curve similar in form to one in which the stable constituents of a soil have been plotted against the depth. This curve has a ratio maximum towards its top which decreases with depth and approaches parallelism with the depth axis, that is, approaches an "equilibrium" stability curve which is indicative of originally unaltered parent material. The curve for Lithologic Unit IV resembles that of Lithologic Unit I; however, because of the more variable lithology, the intense alteration, and the possibility that its upper surface has been eroded, a residual origin for Lithologic Unit IV can be suggested but not substantiated by this analytical method.

It seems rather unique that unaltered, noncarbonate clay samples exhibit a constant ratio of (001) illite line broadening to percent TiO_2. This suggests that rocks of a similar lithology, deposited in a similar environment have an original "equilibrium" state. Such an "equilibrium" state must have been obtained prior to post-depositional alteration, that

is prior to ground-water leaching and soil-forming processes, otherwise the ratio could hardly be expected to remain constant. The rate of "illitization" as well as the rate of TiO_2 concentration would be expected to be vastly different under a given leaching condition.

CONCLUSION

In the section sampled, some lithologies below a coal seam showed evidence of post-depositional alteration. Alteration, most probably the result of ground-water action perhaps during the process of soil formation, is evidenced by concentrations of limonite, by increasing percentages of TiO_2, and by line broadening of the (001) illite reflection which increased with proximity to the surface.

The units directly beneath the coal to a depth of 25 inches were found to be largely free from the effects of ground-water action. They showed relict evidence of abundant plant life and also a variation in (001) illite line broadening and percent TiO_2 similar to that of a fossil soil profile.

Environmental equilibrium between percent TiO_2 and illite degradation (measured by line broadening of the (001) reflection) appears to have been attained for noncarbonate, clay-rich lithologies. Deviations from this equilibrium present a measure of the extent of post-depositional alteration where sediment composition was essentially uniform.

REFERENCES

Brewer, Roy (1964), *Fabric and mineral analysis of soils*, John Wiley and Sons, Inc., 470 p.

Carr, K., Grimshaw, R. W., and Roberts, A. L. (1953), *A hydrous mica from Yorkshire fireclay*, Mineralog. Mag., v. 30, p. 139-144.

Grim, R. E., and Allen, V. T. (1938), *Petrology of Pennsylvanian underclays of Illinois*, Geol. Soc. America Bull., v. 49, p. 1485-1513.

Harrison, J. L., and Murray, H. H. (1959), *Clay mineral stability and formation during weathering*, Proc. 2nd Nat. Conf. on Clays and Clay Minerals, v. 2, p. 144-153.

Huddle, J. W., and Patterson, S. H. (1961), *Origin of Pennsylvanian underclays and related seat rocks*, Geol. Soc. America Bull., v. 72, p. 1643-1660.

Keller, W. D., and Frederickson, A. F. (1952), *Role of plants and colloidal acids in the mechanism of weathering*, Am. Jour. Sci., v. 250, p. 594-608.

Lapham, D. M., and Jaron, M. G. (1964), *Rapid quantitative illite determination in polycomponent mixtures*, Am. Mineralogist, v. 49, p. 272-276.

Nikiforoff, C. C. (1943), *Introduction to paleopedology*, Am. Jour. Sci., v. 241, p. 194-200.

O'Neill, B. J., Jr., Lapham, D. M., Jaron, M. G., Socolow, A. A., Thomson, R. D., and Hamlin, H. P. (1965), *Properties and uses of Pennsylvania Shales and Clays*, Pennsylvania Geol. Survey Rept. M51, 448 p.

Raman, K. V., and Jackson, M. L. (1965), *Rutile and anatase determination in soils and sediments*, Am. Mineralogist, v. 50, p. 1086-1091.

Schultz, L. G. (1958), *Petrology of underclays*, Geol. Soc. America Bull., v. 69, p. 363-402.

Smith, J. V., and Yoder, H. S. (1956), *Experimental and theoretical studies of mica polymorphs*, Mineralog. Mag., v. 31, p. 209-235.

Van Houten, F. B. (1953), *Clay minerals in sedimentary rocks and derived soils*, Am. Jour. Sci., v. 251, p. 61-82.

Velde, Bruce (1965), *Experimental determination of muscovite polymorph stabilities*, Am. Mineralog., v. 50, p. 436-449.

Weaver, C. E. (1965), *Potassium content of illite*, Science, v. 137, p. 603-605.

Wilson, M. J. (1965), *The origin and geological significance of the South Wales underclays*, Jour. Sed. Petrology, v. 35, p. 91-99.

Yoder, H. S., and Eugster, H. P. (1955), *Synthetic and natural muscovites*, Geochim, Cosmochim, Acta, v. 8, p. 225-280.